

# Submillimeter Spectra of Low Temperature Gases and Mixtures

*E.H. Wishnow, H.P. Gush, M. Halpern, I. Ozier*

This article was submitted to NASA Laboratory Astrophysics  
Workshop, NASA-Ames Research Center, Moffett Fields, CA, May  
1-3, 2002

**September 19, 2002**

U.S. Department of Energy

Lawrence  
Livermore  
National  
Laboratory

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
And its contractors in paper from  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
Telephone: (865) 576-8401  
Facsimile: (865) 576-5728  
E-mail: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for the sale to the public from  
U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: (800) 553-6847  
Facsimile: (703) 605-6900  
E-mail: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory  
Technical Information Department's Digital Library  
<http://www.llnl.gov/tid/Library.html>

# Submillimeter Spectra of Low Temperature Gases and Mixtures

E.H. Wishnow

*V-Division, Lawrence Livermore National Laboratory, Livermore, CA USA, 94551*

wishnow@llnl.gov

and

H.P. Gush, M. Halpern, I. Ozier

*Physics Department, University of British Columbia, Vancouver, British Columbia,  
Canada V6T 1Z1*

## ABSTRACT

Submillimeter absorption spectra of nitrogen, nitrogen-argon mixtures, and methane have been measured using temperatures and pressures near to those found in the atmospheres of Titan and Saturn. The experiments show the spectral signature of dimers which will likely appear in far-infrared spectra of Titan that will be obtained by the Composite Infrared Spectrometer (CIRS) onboard the Cassini spacecraft. The recent CIRS spectrum of Jupiter shows far-infrared spectral lines of methane and the corresponding lines are observed in the laboratory. We are extending this work to lower frequencies using a new differential Michelson interferometer that operates over the frequency region 3–30  $\text{cm}^{-1}$ .

## 1. Introduction

We have conducted experiments, and are developing a new spectrometer and absorption cell apparatus, to measure submillimeter spectra of simple gases and gas mixtures. The spectra signatures of dimers is an area of particular interest as these features have been seen in planetary spectra. Dimers are weakly bound pairs of molecules that form stably when the temperature is comparable to the depth of the intermolecular potential. The dimer has a set of vibrational and rotational energy states which depend on the molecules' separation and orientation. Even though the individual molecules that compose the dimer do not possess permanent electric dipole moments, the dimer can possess a dipole moment and transitions between energy states give rise to rotation-vibration spectral lines at low frequencies. The Voyager spectrum of Jupiter shows small  $\text{H}_2\text{-H}_2$  dimer features located near the  $\text{S}(0)$  and

S(1) transitions of hydrogen at 354 and 587  $\text{cm}^{-1}$  respectively (McKellar 1984; Frommhold, Samuelson, & Birnbaum 1984), and the Voyager spectrum of Titan shows features in the same regions which are attributed to the  $\text{H}_2\text{-N}_2$  dimer (Borysow & Frommhold 1986).

## 2. Nitrogen and Nitrogen-Argon Spectra

The left panel of Figure 1 shows a comparison of low temperature  $\text{N}_2$  and  $\text{N}_2\text{-Ar}$  absorbance spectra ( $-\ln(\text{transmission})$ ). The measurements were conducted using a Fourier transform spectrometer and multi-reflection absorption cell cooled with liquid argon or liquid nitrogen (Wishnow, Leung, & Gush 1999). The optical path was 52 m and the spectral resolution was 0.24  $\text{cm}^{-1}$ . The upper curve is from 538 Torr of  $\text{N}_2$  at 78 K (2.54 Amagat) and the lower curve is from a 50/50 mixture of  $\text{N}_2\text{-Ar}$  at 88 K (2.6 Amagat) (Amagat units are a ratio of sample density to Loschmidt's number, the atmospheric number density at STP). The circles are the calculated absorbance for 2.54 Amagat of  $\text{N}_2$  at 93 K based on the previous generation of high pressure, low resolution experimental studies Dore & Filabozzi (1987).

The broad continuum is due to the  $\text{N}_2$  collision-induced translation-rotation spectrum. The rippled structure superposed on the continuum is due to the presence of dimers and it is enhanced in the  $\text{N}_2\text{-Ar}$  spectrum relative to the pure  $\text{N}_2$  spectrum. The dimer structure can only be observed using relatively high spectral resolution and relatively low gas pressures; this structure was not seen in the previous generation of high pressure experiments.

The right panel of Figure 1 shows  $\text{N}_2\text{-Ar}$  spectra with the collision-induced continuum removed. The  $\text{N}_2/\text{Ar}$  mixing ratio, total density, and temperature from top to bottom are: 50/50, 5.2 Amagat, 88 K; 24/76, 3.04 Amagat, 88 K; pure  $\text{N}_2$ , 2.54, 78 K. The detailed structure in the upper two curves is clearly different from the lower, pure  $\text{N}_2$  curve. The amplitude of the ripples is obviously enhanced by the presence of argon; notice that the upper curve and lower curve have the same amount of  $\text{N}_2$  in the gas sample. It is interesting that the minima of the ripples correspond to the rotational transition frequencies of the  $\text{N}_2$  molecule. At frequencies between 35 and 50  $\text{cm}^{-1}$ , the ripples give way to detailed structure indicating that the  $\text{N}_2$  molecule is no longer a free rotator for low  $\text{N}_2$  rotational states. This work has been reported previously (Wishnow, Gush, & Ozier 1996), and it is compared to calculated  $\text{N}_2\text{-Ar}$  spectra (Wang, McCourt, & Le Roy 2000).

The rippled structure is likely to be observed in the spectrum of Titan by the CIRS spectrometer on Cassini. The argon abundance determined spectroscopically can be compared to mass spectrometer measurements made by the Huygens descent probe.

### 3. Methane

Even though the methane molecule is symmetric in the electronic and vibrational ground state, a weak dipole moment arises in a molecule with rotational quantum state  $J > 0$  due to centrifugal distortion. Figure 2 shows the first observation of centrifugal distortion spectral lines below  $80\text{ cm}^{-1}$ . Early CIRS spectra of Jupiter, courtesy of Don Jennings NASA/GSFC, show methane lines in absorption over the range  $60$  to  $110\text{ cm}^{-1}$ . The analysis of the laboratory data is underway to support the interpretation of Jupiter spectra and the anticipated data from Saturn.

### 4. New Spectrometer System

We are developing a new differential Michelson interferometer to study dimer spectra in the frequency region  $3\text{--}30\text{ cm}^{-1}$ . The system has twin light pipe optical cells  $6.11\text{ m}$  long and two  $^3\text{He}$  cooled bolometers. Each detector measures the interferogram that arises from the difference spectrum of cell 1 and cell 2. In principle, if both cells contain the same quantity of  $\text{N}_2$  and argon is added to one cell, the interferogram should be due only to the  $\text{N}_2\text{-Ar}$  dimers.

This work is supported by NSERC of Canada. This work is supported by the NASA Planetary Atmospheres program. This work was performed under the auspices of the U.S. Department of Energy, National Nuclear Security Administration by the University of California, Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

### REFERENCES

- Borysow, A. & Frommhold, L. 1986, ApJ, 303, 495
- Dore, P. & Filabozzi, A. 1987, Canadian Journal of Physics, 65, 90
- Frommhold, L., Samuelson, R., & Birnbaum, G. 1984, ApJ, 283, L79
- McKellar, A. R. W. 1984, Canadian Journal of Physics, 62, 760
- Wang, F., McCourt, F. R. W., & Le Roy, R. J. 2000, J. Chem. Phys., 113, 98
- Wishnow, E. H., Gush, H. P., & Ozier, I. 1996, J. Chem. Phys., 104, 3511
- Wishnow, E. H., Leung, A., & Gush, H. P. 1999, Review of Scientific Instruments, 70, 23

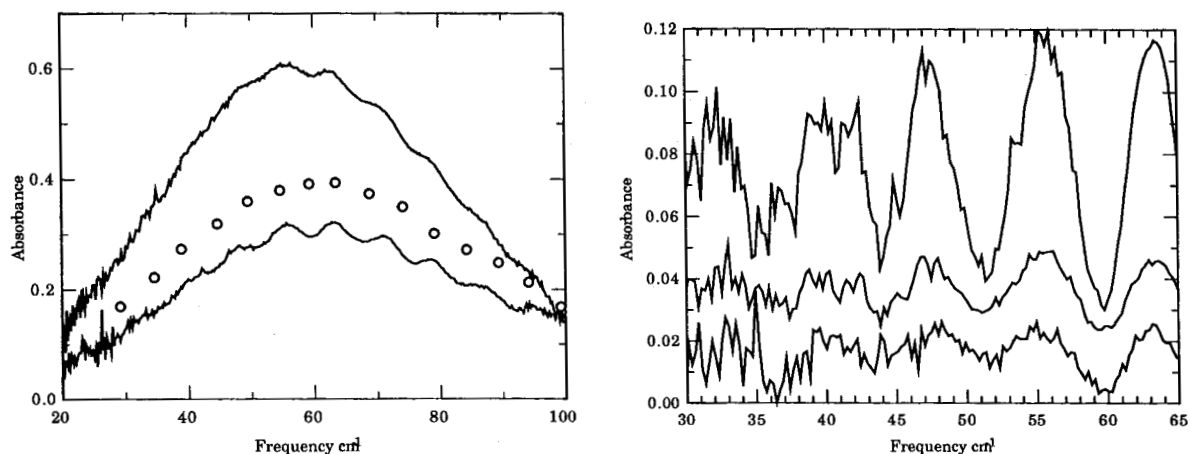


Fig. 1.— Left panel, low temperature  $\text{N}_2$  and  $\text{N}_2$ -Ar spectra. The upper curve is from pure  $\text{N}_2$  at 78 K, the circles are pure  $\text{N}_2$  at 93 K, the lower curve is for a  $\text{N}_2$ -Ar mixture at 88 K; all densities are near 2.5 Amagat (see text). Right panel, baseline removed  $\text{N}_2$  and  $\text{N}_2$ -Ar spectra. The upper curve is a 50/50 mix of  $\text{N}_2$ -Ar; the middle curve is a 24/76 mix of  $\text{N}_2$ -Ar; the lower curve is pure  $\text{N}_2$ . The curves are offset vertically by an arbitrary amount.

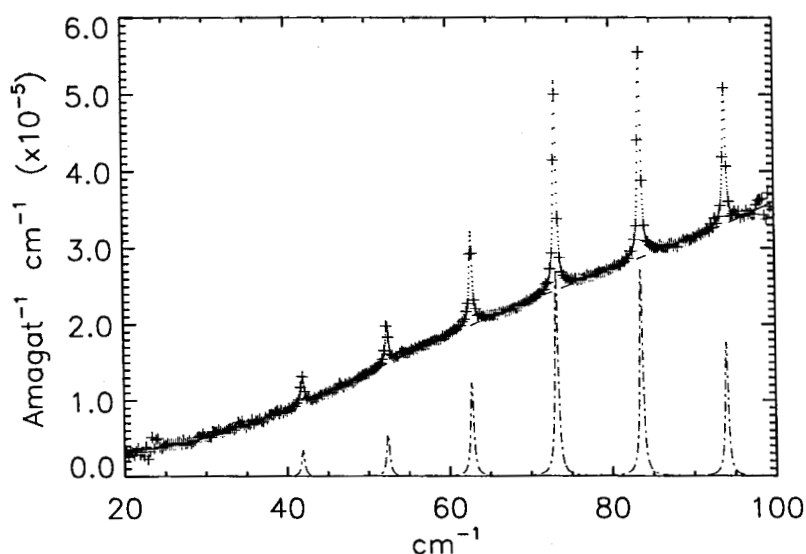


Fig. 2.— The absorption spectrum of methane. '+' are measurements of a 794 Torr methane sample at 113.5 K using a 60 m optical path. The dots are a fit to the data at 10x higher spectral resolution using 6 Lorentzian lines superposed on a quartic continuum; the dot-dash line shows the continuum removed spectrum.